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## Formation of Ordered Silica–Organic Hybrids by Self-Assembly of Hydrolyzed Organoalkoxysilanes with Long Organic Chains

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### ABSTRACT

Various layered hybrid films prepared from organoalkoxysilanes with long organic chains, based on the self-assembly of the hydrolyzed species, are reviewed. Morphological control of transparent and oriented films was achieved by cohydrolysis and polycondensation with tetraalkoxysilanes, followed by dip- or spin-coating. In addition to alkyltrialkoxysilanes, alkyltrimethylmonalkoxy- and alkylmethyldialkoxysilanes were also used as the structural units, implying that the inorganic–organic interface can be designed at a molecular level. In these cases, co-condensation in the precursor solution plays an essential role in the formation of homogeneous and ordered films. Alkenyltriethoxysilanes with terminal C=C bonds were also employed to prepare layered hybrid films. Interlayer chains were polymerized upon UV irradiation, and the resulting films exhibited a significant increase in the hardness if compared with the films before polymerization. Hybrid films thus obtained are a new class of materials and of great interest for a wide range of materials chemistry.

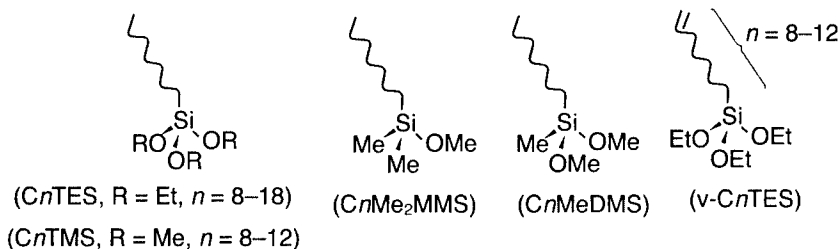
### INTRODUCTION

Organoalkoxysilanes are widely used as structural units to construct a variety of silica-based hybrid materials [1–3]. Because simple sol–gel reactions of alkoxysilanes usually result in the formation of amorphous materials [4], much efforts have been made in the structural control on a nanometer-length scale [5–8]. Such an attempt is of great interest from the possibility to produce novel hybrid materials with unique structures and properties.

Self-organization of organosilane molecules is a promising technique for the construction of ordered hybrid materials. The process relies on the amphiphilic nature of hydrolyzed organosilane molecules containing both hydrophilic silanol groups and hydrophobic alkyl chains. While many studies have focused on the interfacial deposition of alkylsiloxane monolayers [9], researchers have recently shown that the process can be extended to the formation of multilayered hybrids by the reaction in solution states [10–12]. We reported the formation of multi-bilayer aggregates by hydrolysis and polycondensation of alkyltrialkoxysilanes in homogeneous solutions [12]. These are a new class of layered materials consisting of organic two-dimensional arrays and siloxane networks linked by covalent Si–C bonds.

Although the layered hybrids derived from alkyltrialkoxysilanes are obtained as powders, transparent and oriented thin films can be obtained by cohydrolysis and polycondensation with tetraalkoxysilane under well-controlled conditions [13]. This synthetic approach can be extended to the development of a variety of hybrid materials by the molecular design of starting organoalkoxysilane with varied alkyl chain lengths, controlled numbers of the organic groups, and various functionalities in the organic groups.

In this paper, we present a review of the recent developments conducted in our laboratory on the formation of ordered hybrid films derived from the organoalkoxysilane–tetraalkoxysilane systems [14–16]. In addition to the alkyltrialkoxysilane with various chain lengths, alkyltrimethoxysilane and alkylmethyldialkoxysilanes as well as alkenyltrialkoxysilane were used as the starting molecules (figure 1). This approach will lead to the formation of highly organized architectures by a simple sol–gel route using various organoalkoxysilanes.



**Figure 1.** Organoalkoxysilanes used in this study.

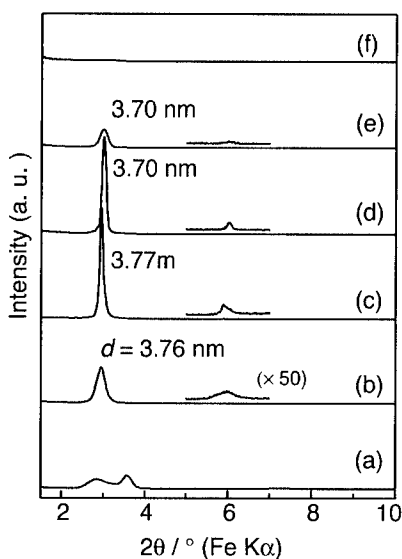
## LAYERED HYBRID FILMS DERIVED FROM $C_n$ TES-TEOS SYSTEMS

Precursor solutions were prepared by cohydrolysis and polycondensation in the  $C_n$ TES-TEOS-EtOH-H<sub>2</sub>O-HCl system [14]. The <sup>1</sup>H NMR spectra of the reaction mixtures revealed that the signals due to ethoxy groups (SiOCH<sub>2</sub>CH<sub>3</sub>, at around 3.8 ppm) almost disappeared within the first period of 15 min. The <sup>29</sup>Si NMR spectra of the solution in the C18TES-TEOS system revealed that the signals assigned to the monomeric species of both alkoxysilanes disappeared after the reaction at 40 °C for 90 min. Although the signals due to oligomeric species were not clearly resolved, the co-condensation between  $C_n$ TES and TEOS should occur because sufficient evidences have already been reported in similar systems [17,18].

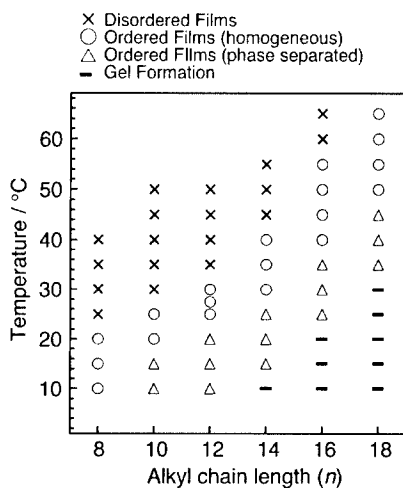
Thin films were deposited on glass substrates by dip-coating. However, the structural ordering and the macroscopic homogeneity of the films depended largely on the alkyl chain length as well as the solution temperature during the deposition. In the C10TES-TEOS system, transparent films exhibiting a sharp diffraction peak ( $d = 3.48$  nm) were formed at around room temperature (20–25 °C). The layered structure of the film was confirmed by TEM (not shown). Although the films prepared at lower temperatures (10 and 15 °C) also exhibited sharp diffraction peaks, they were not homogeneous and the  $d$  values were rather variable. In contrast, the deposition at higher temperatures up to 30 °C resulted in the formation of homogeneous films with a disordered nanostructure. Similar trends were also observed for the systems with  $n = 8$  and 12.

In the case of  $n \geq 14$ , neither transparent nor well-ordered films were deposited from the solution at around room temperature. Figure 2 shows the variation in the XRD pattern of the hybrid films in the C14TES-TEOS system. The films obtained at around room temperature exhibited very broad peaks. However, the intensity of the peaks progressively increased as the solution temperature increases, and transparent and highly ordered films were obtained at 30–35 °C. The effect of the solution temperature was more clearly observed for the systems with  $n = 16$  and 18. In these cases, well-ordered films with sharp and intense peaks were formed at 40–45 °C and 55–60 °C, respectively.

The incorporation of the Q units in the  $C_n$ TES-derived hybrids contributed to the thermal stability. The layered hybrid derived from C18TES alone melted into an amorphous state upon heating above ~110 °C [12]. In contrast, the layered product



**Figure 2.** XRD patterns of the hybrid films in the C14TES-TEOS system prepared at various temperatures: (a) 20 °C, (b) 25 °C, (c) 30 °C, (d) 35 °C, (e) 40 °C, and (f) 45 °C.



**Figure 3.** Variation of the products derived from the  $C_n$ TES-TEOS systems ( $n = 8-18$ ) depending on the solution temperatures.

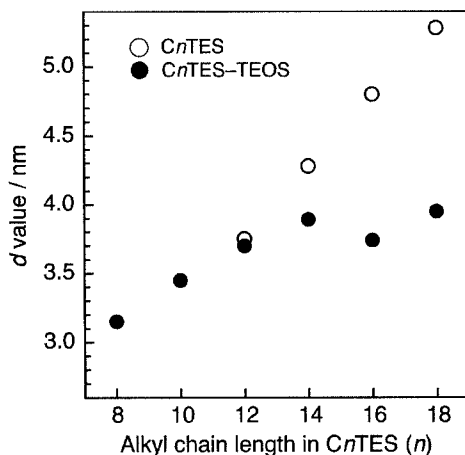
derived from the C18TES-TEOS system retained the structure even at 170 °C, suggesting that the product was comprised of more stable siloxane networks.

Figure 3 summarizes the variation of the nanostructure and the macroscopic morphology of the resulting hybrids depending on the solution temperature during the film formation. Transparent and ordered films are formed at higher temperatures with increasing chain length, suggesting that the self-assembly of alkylsiloxane oligomers depend essentially on the solution temperature. When a substrate is withdrawn from the reaction mixtures, silicate species in the solutions are concentrated by the evaporation of the solvent, and finally polycondensed to form siloxane networks. The formation of oriented multilayered films requires uniform and continuous organization, presumably from solid-liquid and liquid-vapor interfaces, during this coating process. In the cases of  $C_n$ TES with longer chains ( $n \geq 14$ ), the films deposited at lower temperatures exhibited a less-ordered structure. This behavior is probably attributed to the random nucleation of the layered aggregates caused by a slight decrease in the temperature as well as the evaporation

of the solvent during the film formation. The suppression of the segregation of the layered aggregate appears to play an important role in the formation of oriented films. In all the systems, further increase in the deposition temperature caused the structural disordering and eventually led to amorphous films. This is explained by the general behavior of amphiphilic assemblies that become isotropic states at higher temperature. The films may be solidified by the siloxane formation prior to the self-organization.

Figure 4 represents the basal spacings of the well-ordered films as a function of the alkyl chain length. For comparison, the  $d$  values for the layered hybrids derived from  $C_n$ TES ( $n = 12-18$ ) alone are also shown. As we reported previously, the products derived from  $C_n$ TES alone are comprised of a bilayer structure with *all-trans* chains almost perpendicular to the siloxane layers [12]. In contrast to the linear relationship in these products, the  $d$  spacing of the films increases continuously in the range of  $n = 8$  to 14, but decreases between  $n = 14$  to 16. It is reasonable to assume that the thickness of the siloxane layer is almost constant independent of the chain lengths, because the TEOS/ $C_n$ TES ratio is identical in all the systems. Therefore, the above behavior should be attributed to the variation in the conformation and/or the packing arrangement of the interlayer alkyl chains depending on the alkyl chain length.

The difference in the conformations of the alkyl chains in the films was confirmed by  $^{13}\text{C}$  CP/MAS NMR. The  $^{13}\text{C}$  signals ascribed to the interior methylene carbons appear at 30 ppm for  $n = 8-14$ , suggesting the presence of *gauche* conformers. However, the



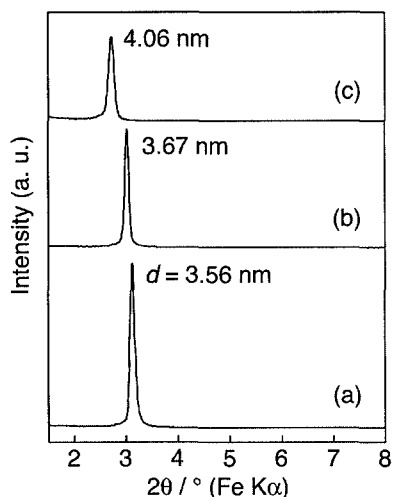
**Figure 4.** Variation in the  $d$  values as a function of the number of carbon atoms in the alkyl chain: The layered hybrid films derived from the  $C_n$ TES-TEOS systems (filled circles) and the layered hybrids derived from  $C_n$ TES alone (open circles).

relative intensity of the signal at 33 ppm, indicative of the chains in *all-trans* conformations, increases as the chain length increases to  $n = 16$  and  $18$ .

The packing arrangements of the interlayer chains can be divided into two types, i.e. interdigitated monolayer and bilayer structures, according to the representative models for amphiphilic lamellar phases [19]. In the cases of  $n = 8-12$ , the alkyl chains are supposed to adopt a bilayer structure with disordered state, based on our study on the layered hybrid films derived from  $C_n\text{TMS}$  ( $n = 8-12$ )-TMOS systems [13]. However, in the cases of  $n = 16$  and  $18$ , the observed  $d$  spacings appear to be too small for the similar bilayer structures, considering that the chains are longer and take more extended states. Indeed, the  $d$  value of the film in the C18TES-TEOS system is considerably smaller than that of a bilayer structure derived from C18TES alone (figure 4), although there is no significant conformational difference in both of the products. It is considered that the alkyl chains are arranged in an interdigitated monolayer with a rather ordered state. Such interlayer structures are also reported for the alkylsilylated derivatives of crystalline layered polysilicates [20,21], and may arise from the increases in the distance between alkylsilyl groups due to the presence of co-condensed Q units.

### **LAYERED HYBRID FILMS DERIVED FROM $C_n\text{TMS}$ -, $C_n\text{MeDMS}$ -, AND $C_n\text{Me}_2\text{MMS}$ -TMOS SYSTEMS**

In these systems, hybrid films were prepared by cohydrolysis and polycondensation of  $C_n\text{TMS}$  ( $n = 8, 10, 12$ )-TMOS-THF- $\text{H}_2\text{O}$ -HCl mixtures, followed by spin-coating on glass substrates [15]. As shown in figure 5, the XRD patterns of the hybrid films derived from the C10TMS-, C10MeDMS-, and C10Me<sub>2</sub>MMS-TMOS systems showed sharp diffraction peaks with the  $d$  spacings of 3.56, 3.67, and 4.06 nm, respectively. The structural ordering and the macroscopic morphology of the films are strongly affected by the reaction time in the precursor solutions. The solutions at the earlier stages of the reactions afford inhomogeneous films with phase separated morphologies. On the other hand, further reactions in the precursor solutions caused the disordering of the nanostructures, and finally led to the formation of amorphous films. Controlled reaction in the precursor solutions was needed for the formation of well-ordered and transparent hybrid films.



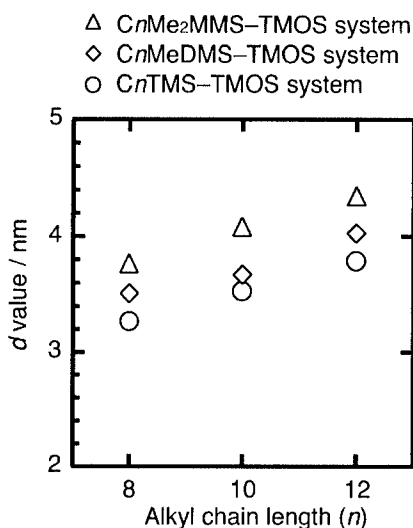
**Figure 5.** XRD patterns of the hybrid films derived from (a) C10TMS-, (b) C10MeDMS-, and (c) C10Me<sub>2</sub>MMS-TMOS systems.

The TEM images of the ordered films showed well-defined stripes due to the lamellar structures, and the periodicities agree closely with the  $d$  spacings measured by XRD. The layered structures of these films were also confirmed by the structural collapse upon calcination at 450 °C for 6 h to remove organic constituents.

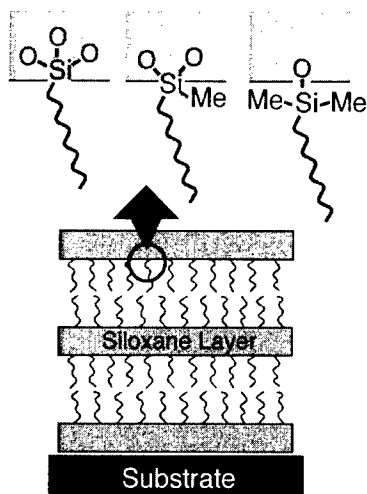
The formation of siloxane networks in the films was confirmed by <sup>29</sup>Si MAS NMR. The spectra for all the systems showed the signals assigned to the Q<sup>2</sup> (−90 ppm), Q<sup>3</sup> (−100 ppm), and Q<sup>4</sup> (−110 ppm) units derived from TMOS. In addition, the signals due to the organosiloxane units derived from C10TMS, C10MeDMS, and C10Me<sub>2</sub>MMS are observed at the T<sup>2</sup> (−55 ppm) and T<sup>3</sup> (−65 ppm), D<sup>1</sup> (shouldered peak at −10 ppm) and D<sup>2</sup> (−16 ppm), and M<sup>1</sup> (13, 7 ppm) regions, respectively.

Similar hybrid films were prepared when the alkyl chain lengths in alkylmethoxysilanes were 8 and 12. The formation of ordered films required longer reaction time in the precursor solution with increasing chain length. This is in part ascribed to the difference in the condensation rate depending on the chain length. In this manner, the reaction time in the precursor solution was optimized depending on the number of methoxy groups and alkyl chain lengths. Figure 6 shows the relationship between the  $d$  values of the resulting hybrid films and the alkyl chain lengths of the alkylmethoxysilanes used. The  $d$  value increases continuously with increasing chain lengths and exhibit larger value as the number of methoxy groups decreases.





**Figure 6.** Variation in the  $d$  values of the hybrid films as a function of the alkyl chain length in the alkylmethoxysilanes.



**Figure 7.** Proposed structural models for the hybrid films derived from  $C_n$ TMS-,  $C_n$ MeDMS-, and  $C_n$ Me<sub>2</sub>MMS-TMOS systems.

The structural models for the hybrid films are schematically illustrated in figure 7. The films have multilayered structures consisting of a bilayer arrangement of alkyl chains that are covalently attached to siloxane layers. The observed difference in the  $d$  value with varying the number of methoxy groups in the starting alkylmethoxysilanes (figure 6) is probably attributed to the variation in the interfacial structures. It is supposed that the trialkoxysilyl groups are in part integrated into the siloxane networks due to their cross-linking abilities, while the substitution of methyl groups for methoxy groups results in the grafting on the external surface of silica layers.

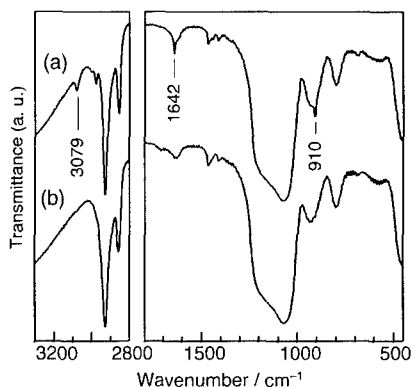
In the present system, co-condensation between alkylmethoxysilanes and TMOS in the precursor solution plays a crucial role in the formation of ordered hybrid films. This is supported by the fact that neither transparent nor ordered films were obtained by the hydrolysis and polycondensation of alkylmethoxysilane alone. In the  $^{29}\text{Si}$  NMR spectra of the precursor solutions, the signals due to monomeric species almost disappeared and those of the oligomeric species including substantial amounts of co-condensed units were observed. These results provide a strong evidence that the origin of the self-assembly in

this system is quite different from that of the conventional single-component systems using alkyltrialkoxysilanes alone [12]. The alkylsiloxane oligomers formed by the co-condensation can be regarded as amphiphilic molecules containing both hydrophobic alkyl chains and hydrophilic silanol groups. We suppose that the construction of ordered films relies on the self-assembly of these oligomeric species by the rapid evaporation of the miscible solvent during the spin-coating procedure.

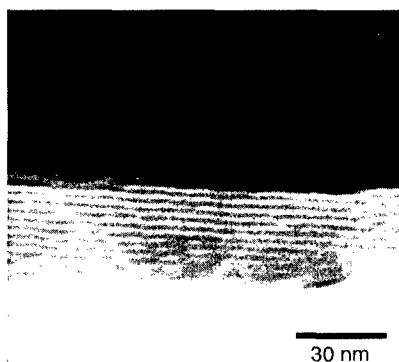
### **LAYERED SILICA/ORGANIC POLYMER HYBRID FILMS DERIVED FROM $v$ - $C_n$ TES-TEOS SYSTEMS**

Multilayered hybrid films were also prepared from  $v$ - $C_n$ TES-TEOS-EtOH-H<sub>2</sub>O-HCl mixtures [16]. The films before UV irradiation showed sharp diffraction peaks with the  $d$  spacing of ca. 3.0–3.6 nm, depending on the chain lengths. The films are considered to have a bilayer arrangement of alkenyl chains, because the  $d$  spacings of the films are similar to those of the films derived from  $C_n$ TES-TEOS systems (see figure 4). The IR spectrum of the  $v$ -C8TES-derived film before the UV irradiation (figure 8a) shows the absorption bands due to the siloxane framework (1000–1200  $\text{cm}^{-1}$ , 450  $\text{cm}^{-1}$ ) and the terminal double bonds in the organic groups at 3079  $\text{cm}^{-1}$  (=CH stretching), 1642  $\text{cm}^{-1}$  (C=C stretching), and 910  $\text{cm}^{-1}$  (=CH<sub>2</sub> out-of-plane deformation). These results suggest that the films are composed of lamellar structures containing vinyl functionalities within the interlayers.

The film exposed to the UV light still retained the structural order with a slight decrease in the  $d$  value in the XRD pattern. As shown in figure 9, the TEM image of the film derived from the  $v$ -C8TES-TEOS system shows well-defined stripe patterns whose periodicity corresponds to the  $d$  spacing determined by XRD. The polymerization of organic chains was evidenced by the substantial decrease in the IR absorption bands ascribed to the terminal double bonds (figure 8b). Because the interlayer organic chains in this system appear to adopt a bilayer structure, polymerization should have proceeded either within layers or between adjacent layers. The resulting hybrid film exhibited a remarkable increase in the hardness and the scratch resistance if compared with the film before the organic polymerization.



**Figure 8.** FT-IR spectra of the films derived from the v-C8TES-TEOS system (a) before and (b) after the UV irradiation.



**Figure 9.** TEM image of the hybrid film derived from the v-C8TES-TEOS system after the UV irradiation. (The film was powdered for the observation.)

All these results indicate the formation of inorganic-organic hybrid films with a lamellar structure in which the siloxane layers and the organic polymer are linked by Si-C bonds. With regard to the silica-organic polymer hybrids, intercalation of organic polymers into the interlayer spaces of crystalline layered silicates has attracted much attention for the possibility to provide new properties [22]. Covalent linking between organic moieties and silica interlayers can also be attained by using a silane coupling agent such as  $\gamma$ -methacryloxypropyltrimethoxysilane [23]. However, the present approach is quite different in utilizing the molecular self-assembly of organoalkoxysilane-tetraalkoxysilane system, which enabled the morphological control into the transparent and oriented thin films.

## CONCLUSIONS

We have presented the formation of multilayered hybrid films consisting of alternating organic and siloxane layers by the sol-gel reaction of a series of organoalkoxysilanes and tetraalkoxysilane. This approach is quite simple and effective for the construction of ordered hybrids with precisely controlled nanostructures, macroscopic homogeneities, and compositions. The introduction of tetraalkoxysilane contributes to the

morphological variation and increases the thermal stability that could not be attained by hydrolysis and condensation of alkyltrialkoxysilane alone. It is of great interest that the ordered hybrid films were also obtained from alkyltrimethoxysilane and alkylmethyldimethoxysilane in the presence of TMOS. In these systems, co-condensation between alkylmethoxysilane and TMOS in the precursor solutions is essential for the self-organization. The overall results provide an access to the generalized synthesis of ordered hybrid films utilizing various organoalkoxysilanes with hydrophobic organic groups.

## ACKNOWLEDGMENTS

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